

EFFECT OF CHEMICAL COMBINATION ON THE ASYMMETRY OF THE $K\alpha$ LINES OF COBALT

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ABSTRACT. The asymmetry indices of the $Co K\alpha_1$ and $K\alpha_2$ lines have been determined for cobalt metal and some of its divalent and trivalent compounds and complexes. The X-ray lines were excited by the fluorescence technique and were registered using a 40 cm bent crystal spectrograph. It has been observed that the indices of asymmetry for both the lines are progressively reduced as one goes from cobalt metal to $Co(II)$ and $Co(III)$ compounds. It has been shown that the asymmetry index depends upon the number of $3d$ electrons in any substance. The surroundings of the central atom, on the other hand, do not seem to play any significant role in the change of the asymmetry index. X-ray fluorescence spectroscopy can therefore be used to determine unknown valencies in complexes of transition metals. The change in the asymmetry of these lines has been attributed to exchange polarisation effect.

INTRODUCTION

The effect of chemical combination on the width and the asymmetry of the $K\alpha_1$, α_2 , lines has been studied in the thirties by many workers (Bearden and Shaw, 1935; Roseberry and Bearden, 1936; Orbert and Bearden, 1938). Recently Meisel and his coworkers (1961, 1962, 1962, 1965, 1965) have shown fresh interest in this problem and have studied in detail the shape of the $K\alpha$ lines of some transition metals of the first series in a large number of compounds and complexes. We thought it worthwhile to study the asymmetry of these lines from two points of view, namely, (1) the effect of valency and (2) the effect of surroundings of the central metal atom emitting the radiation. In this paper we report the results of our investigations carried out with this view on the K lines of some compounds and complexes of cobalt.

EXPERIMENTAL

It is well known that the chemical composition of a substance changes during excitation by direct electron bombardment in an X-ray tube. We have, therefore, employed in this work the technique of fluorescence for exciting the X-ray lines. The general experimental arrangement is shown schematically in fig. 1.

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A Philips sealed X-ray tube with tungsten target was employed for the generation of the primary X-rays. It was operated at 25 KV and 15 ma. The spectra were registered on a 40 cm bent crystal spectrograph, designed and constructed in the Poona University Central Workshop. The (100) planes of a well tested mica crystal were used to record the spectra, which were photographed on Agfa ultra-violet plates. By giving exposures between 90 to 100 hours it was possible to obtain the spectral lines with photodensities satisfying the necessary condition for linear relationship between S , the photodensity and the intensity I . Microphotometer records of the plates were obtained with magnification 50 on a Moll microphotometer.

The fluorescent targets for solid substances were made by pressing their fine powders into a rectangular cavity in a perspex sheet. The samples were then covered by cellophane tape for protection from moisture.

The preparation of cells for obtaining fluorescence spectra of substances in the liquid state presents considerable difficulty. It is necessary to use a cell which will not be attacked by the solution and whose walls will not appreciably absorb the primary and the fluorescent radiations. The cells in this work were prepared by putting the solution between two thin films of celluloid separated by a U shaped perspex sheet.

The fluorescent targets thus prepared were mounted on a metallic attachment which was screwed on the shield of the X-ray tube as shown in fig. 1. With this

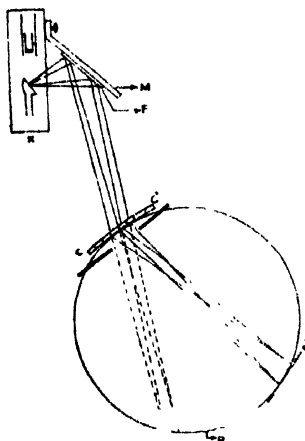


Fig. 1

arrangement it is possible to keep the fluorescent targets very close to the X-ray tube which is necessary because the intensity of the fluorescent radiation is very weak.

RESULTS AND DISCUSSION

It is well known that microphotometer traces do not give, in general, the true intensities directly. It is, therefore, necessary to convert the microphotometer curves into true intensity curves, which was carried out by adopting the usual procedure of determining the photodensities (Blokhin, 1962). The apparent intensities of a large number of points, situated at a distance of 1 mm from each other on every microphotometer trace, were first converted into true intensities and were subsequently plotted on graph papers. One of the typical curves obtained by this method for cobalt metal is shown in fig. 2. This curve (as well as all the others for the compounds and complexes) has not been corrected for the

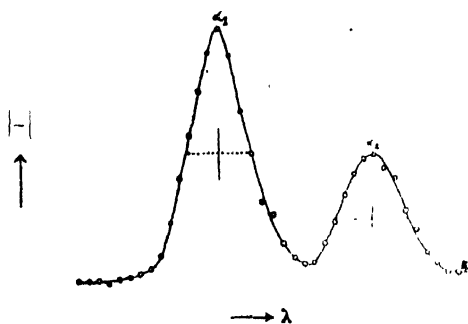


Fig. 2

finite resolving power of the X-ray spectrograph. However, it can be safely assumed that instrumental broadening would not appreciably affect the asymmetry indices in which we are primarily interested in this work, since this broadening effect would occur on both sides of the line profiles.

It may be remarked here that the earlier workers have used either ionization chambers or G.M. counters for recording the X-ray lines. These detection techniques, although more sensitive and quicker, do not give the exact position of the maximum ordinate of a spectral line. In this respect, our procedure in which the position of the maximum ordinate is determined with greater certainty, is superior.

The index of asymmetry of an X-ray line has been defined (Allison, 1933) as the ratio of the part of the full width at half maximum lying to the long wavelength side of the maximum ordinate to that on the short wavelength side. In table 1 are given the results on the asymmetry of the $K\alpha_1$ and the $K\alpha_2$ lines of cobalt obtained in this investigation. The results of Parratt (1936) and Bearden and Shaw (1935) are also included in this table for comparison. Our values of the asymmetry index for both these lines for the metal agree fairly well with those given by these workers.

It will be seen from table 1 that $K\alpha_1$ and $K\alpha_2$ lines which are asymmetric in the case of cobalt metal, tend to become more or less symmetric in compounds and

omplexes. This change does not depend upon the co-ordination number of cobalt in the compounds and complexes. It can therefore be concluded that the surroundings of the central atom do not play any significant role in the change of the asymmetry index.

It can also be seen in table I that the asymmetry index decreases progressively as one goes from cobalt metal to Co (II) and Co (III) compounds. This decrease appears to be more or less regular, except in the case of the $K\alpha_2$ line of pink cobalt chloride. The low value of the asymmetry index of this compound seems to be rather exceptional.

The observed reduction in the asymmetry index seems to be linked with the number of electrons in the $3d$ shell. In cobalt metal the d band contains 8.28 electrons per atom (Goodenough, 1963) while in Co (II) and Co (III) complexes there are 7 and 6 electrons respectively in the d shell. The average values of the asymmetry indices for the $K\alpha_1$ line are 1.380, 1.052 and 0.934 for cobalt metal and the divalent and the trivalent complexes respectively. For the $K\alpha_2$ line the average values are 1.297, 1.023 and 0.93. The observed ratios of the asymmetry indices for both the $K\alpha_1$ and $K\alpha_2$ lines agree remarkably well with the proportionality of the number of electrons in the $3d$ shell (8.28 : 7 : 6). This relationship has been established for the first time in this work.

TABLE I
Experimental data on index of asymmetry

	Co- ordination number	Index of Asymmetry	
		$K\alpha_1$	$K\alpha_2$
1. Cobalt metal (Authors)		1.380	1.297
" " (Parratt)		1.440	1.300
" " (Bearden & Shaw)		1.360	1.290
2. Cobalt Chloride (blue)	4	1.07	1.05
3. Cobalt Chloride (pink)	6	1.05	0.75
4. Diquinolinium Cobalt (II) Chloride	4	1.07	1.02
5. Diquinolinium Cobalt Chloride (pink) (Liquid)	6	0.95	0.92
6. Cobalt (II) Oxinate (anhydrous)	4	1.02	1.01
7. Cobalt (II) Oxinate (hydrous)	6	1.05	1.01
8. Cobaltic (III) Oxide Co_2O_3	6	0.95	0.93
9. Hexammino Cobalt (III) Chloride $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$	6	0.92	0.94
10. Sodium Cobaltinitrite (III) $\text{Na}_3\text{Co}(\text{NO}_2)_6$	6	0.93	—
11. Aqua Pentaammino Cobaltic (III) Oxalate $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]_2(\text{C}_2\text{O}_4)_3$	6	0.92	—

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The modification of the wavefunctions of the spin up and spin down $1s$ electrons owing to exchange polarization effects with the unpaired $3d$ electrons has been of considerable interest in recent years (Freeman and Watson, 1965). The present asymmetry also seems to arise from such exchange polarisation effects. Assuming that the polarisation of the p orbitals involved in the emission of the $K\alpha_1, \alpha_2$ lines is negligible, one can attribute the observed asymmetry of these lines to the polarisation of $1s$ up and $1s$ down orbitals. A detailed study of the asymmetry index of a large number of complexes in various transition metals would therefore reveal the extent to which the $1s$ shell gets polarised. Theoretical work in this direction has been undertaken by Dr. K. P. Sinha of the National Chemical Laboratory, Poona and would be reported later. X-ray spectroscopy can thus be a valuable tool for the measurement of the exchange polarisation, complementary to Mössbauer and EPR techniques.

Another important aspect of this investigation is that this method can be used to determine unknown valencies in compounds and complexes. We can cite here the example of the pink solution of diquinolinium cobalt chloride. To our knowledge the valency of cobalt in this complex has not yet been determined. From the asymmetry index, it seems that the valency of the cobalt atom in this complex is three.

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